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# The limit of superheat of liquids

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**Abstract** : Physics of superheated liquid state and measurement of the limit of superheat is an interesting subject of study for a long time A New method of finding the limit of superheat of liquids has been presented here The superheated liquids are in the form of drops suspended in dust free gel The temperature of the superheated liquids were increased very slowly from room temperature to the critical temperature of the liquid The nucleation was detected by a sensitive piezo-electric transducer, from which the signal was amplified, and fed to a comparator and then coupled to a multi channel analyser (MCA) for noting the data in a multi channel scaling (MCS) mode The results show reasonable agreement between the theory and the experiment

**Keywords** : Nucleation, refrigerant-liquid, superheat.

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## 1. Introduction

Superheated liquids are liquids which exist at temperature above their equilibrium boiling point at the system pressure. These liquids are metastable in the thermodynamic sense and can be nucleated to form vapour by homogeneous nucleation or by presence of heterogeneous nucleation sites such as gas pockets, vapour bubbles, solid impurities or by the deposition of energy by ions, charged particles, neutron *etc*. In practice, a liquid cannot be superheated up to the critical temperature, there is a limit to the maximum attainable superheat temperature for any given liquid. This limit is called the 'limit of superheat of the liquid' $T_{sl}$ and this temperature has a characteristic value for a particular liquid. In addition to its importance in basic science, the knowledge of $T_{sl}$ is important in a number of industrial operations where a hot, nonvolatile liquid comes in contact with a cold volatile liquid. If the temperature of the hot liquid reaches to the limit of superheat of the cold liquid, explosive boiling would result. This explosive boiling may initiate shock waves that can damage equipment and injure personnel in the vicinity of the blast [1]. The study of $T_{sl}$ has got another importance after the discovery of bubble chamber [2] and superheated drop detector (SDD) [3]. The operation of these detectors depends on the ambient temperature of the sensitive liquid which is in superheated state. In fact, the threshold energy of the incident beam decreases as the degree of superheat of the liquid. As an example, the principle of neutron spectrometry is the manifestation of this property of threshold energy variation with temperature [4,5]. The threshold energy for detection is therefore limited by the limit of degree of superheat of the liquid. The limit of superheat of liquids can be estimated from theory or can be measured from experiment. But the experimental results reported so far are not in good agreement with the theoretical values. Several authors such as Wismer [6], Harvey *et al* [7], Glaser [2], Briggs [8], Wakeshima and Takata [9] and Basu and Sinha [10] *etc*. have tried to find out the limit of superheat of liquids. Sinha and Jalaluddin [11] has developed an experimental method to find out the $T_{sl}$ by observing the nucleation at the solid-liquid interfaces and it is a practical method of studying the effect of varying the nature of the interfaces on the superheat of liquids. In the present work, a new method of finding the $T_{sl}$ for homogeneous nucleation has been presented for the liquids used in superheated drop detectors where the superheated samples used are homogeneous suspension of superheated drops of refrigerant liquid (having low boiling temperature) in a visco-elastic gel medium.

## 2. Theoretical calculation of limit of superheat

The limit of superheat can be estimated either from the thermodynamic stability theory or from the analysis of the dynamics of the formation of the critical sized vapour embryos. From Van der Waals equation of state, this limit of superheat can be expressed by [10]

$$t_m = \frac{27T_c}{32} \tag{1}$$

where $t_m$ is the limit of superheat of the liquid. For mathematical simplicity, this has been calculated by considering the operating pressure to be zero. For the operating pressure = 1 atmosphere, $t_m$ will be slightly greater than the above value [10].

Among the other ways of finding limit of superheat $T_{sl}$, Reid [1] has given a simple empirical formula from thermodynamics as follows

$$T_{sl} = T_c\left[0.11(P/P_c)+0.89\right], \tag{2}$$

where $T_{sl}$ is the thermodynamic limit of superheat, $T_c$ is the critical temperature, $P_c$ is the critical pressure and $P$ is the ambient pressure.

Another technique for estimating $T_{sl}$ involves detailed considerations of the sequential rate processes to form vapor embryos in a superheated liquid [1]. For the present analysis, the theoretical values of limit of superheat were calculated by using eq. (1) and (2).

## 3. Experiment

The experiment was carried out with superheated liquids of R12 ($CCl_2F_2$, b.p. –29.79°C), R114 ($C_2Cl_2F_4$, b.p. 8.92°C) and R502 (azeotrope of R22, $CHClF_2$, 48.8% and R115, $C_2ClF_5$, 51.2% by weight, b.p. –45.6°C). The superheated drops were suspended in dust free visco-elastic degassed ultrasonic gel. This avoids the heterogeneous nucleation sites and also minimizes the nucleation at the solid-liquid interfaces. The vapour nucleation in superheated drops was observed by the response of a piezo-electric transducer, the signal from which was amplified, compared with an adjustable threshold (of value just above the noise floor) and then shown in the digital display. All these parts are included in a compact instrument called Drop counter developed in our laboratory. The signals from the Drop counter were recorded in a multichannel analyser (MCA) in the multichannel scaling mode (MCS). The schematic diagram of the apparatus is shown in Figure 1. A glass vial containing the superheated drops in gel was placed inside a glass beaker containing degassed gel. The gel in the beaker was due to the acoustic coupling between the superheated drops in the vial and the transducer. Above the sample in the vial there was some gel and the thermometer was immersed in this gel. To avoid nucleation at the bulb, the thermometer has not been inserted inside the sample. The vial was wrapped by a heating coil covering the gel and sample. The beaker containing the vial was coupled with a piezo-electric transducer using some aquasonic gel. Each time a drop nucleates, there is an acoustic pulse produced and the transducer converts this acoustic pulse into electric signal which is counted by a Drop counter. The temperature of the sample has been increased from room temperature to the critical temperature of the liquid and the count rates ($dN/dt$) were recorded in MCA. At the limit of superheat, $1/N(dN/dt) = 1$.

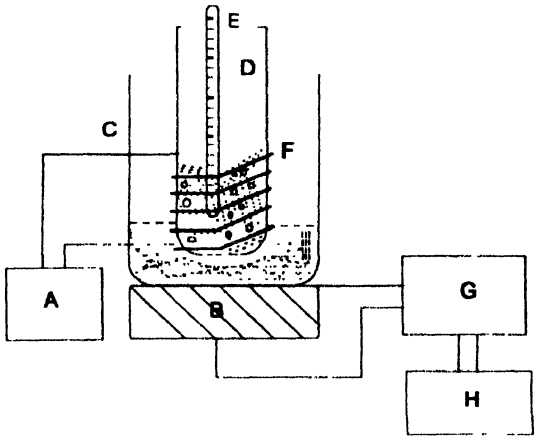


**Figure 1.** Schematic diagram of the experimental arrangement A autotransformer, B piezoelectric transducer, C glass beaker, D glass vial containing sample, E thermometer, F heating coil, G drop counter H multichannel analyser

## 4. Discussion

The results are presented in Table 1. The superheated state is a metastable state of the liquid and undergoes phase transition to stable state by the small perturbations like thermal shock or any mechanical disturbances *etc*. Therefore while observing limit of superheat of liquids, the temperature of this superheated state should be increased slowly so as to avoid any heat shock. In a separate experiment, we observed that the superheated drops become more fragile under heat shock and nucleate rapidly under small perturbations. The calculated values of limit of superheat obtained from the empirical formula (2) are much higher than our observed values. It is to be noted in this connection that the above formula is valid for the homogeneous nucleation which excludes various interfaces with different surface energies *e.g.* gas-liquid, liquid-liquid, solid-gas and it is not clear whether the

**Table 1.** Comparison of critical temperatures, theoretical and experimental values of limit of superheat of the three refrigerant liquids.

| Liquids | R12 | R114 | R502 |
|---|---|---|---|
| Critical Temp. (°C) | 111.5 | 145.7 | 90.1 |
| $t_m$ (°C) (Van der Waals) | 94 08 | 122.93 | 76 02 |
| $T_{sl}$ (°C) [1] | 99.53 | 131.76 | 80.42 |
| $T_{sl}$ (°C) (Expt.) | 80 | 120.5 | 44.5 |

thermodynamic limit of superheat is reachable for the case of the liquid to vapour transition as has been pointed out by Lo [12]. Furthermore, this deviation of experimental observation and theoretical prediction is not unusual as has been observed by Basu and Sinha [10] and Temperley [13].

Basu and Sinha [10] has noted that the difference between the theoretical and experimental values of the limit of superheat increases with the molecular weight of the liquid. They have plotted a graph representing variation of this deviation with the molecular weight of the liquid, the deviation increasing with the molecular weight of the liquid. According to this graph, the above difference (between equation of state and experiment) for molecular weight 120.92 corresponding to R12, is expected to be 33.67°C while the observed deviation from our experiment is 14.08°C, thus approaching closer to the theoretically predicted value.

The difference between the theoretical and the experimental results increases with the degree of superheat of the liquid. This is due to the fact that the sensitivity of the superheated liquids increases with the degree of superheat of the liquid and therefore a very small perturbation can initiate the nucleation in such state. So it becomes difficult to reach closer to critical temperature for the liquids with high degree of superheat as observed for R502, since at a given temperature the degree of superheat of R502 is the maximum among the three liquids used here. Another reason for the large deviation of experimental observation and theoretical prediction may be that R502 is not a pure liquid, it is a mixture of two liquids (R115 and R22) and some interactions among the components of the mixture may take place during the increase of temperature.

One can not reach upto critical temperature and the challenge is how close one can reach to the critical temperature. In the present experiment, it is possible to reach about 90% of the critical temperature for all the liquids studied while for several liquids studied by Basu and Sinha [10], 75.5% to 86.8% of critical temperature have been reached. Our future plan is to extend this improved method of measuring limit of superheat for more common liquids.

## 5. Conclusion

Since we have been able to reach more close to the theoretical limit of superheat and critical temperature of the liquid experimentally, we may conclude that the present experimental technique is superior to the others. It is also to be noted in this connection that in all measurements done so far, nucleation was observed visually whereas the present measurement utilises digital electronics in observing the nucleation.

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